

CARBONATES

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INTRODUCTION

There are approximately 150 carbonate minerals that occur in nature; however, most of these carbonates are relatively rare. The most common rock-forming carbonates are calcite [CaCO_3] and dolomite [$\text{CaMg}(\text{CO}_3)_2$], which account for over 90% of natural carbonates (1). Calcite, dolomite, siderite [FeCO_3] and ankerite [$\text{Ca}(\text{Mg,Fe})(\text{CO}_3)_2$] are the most common carbonates that occur in sedimentary environments (2). Carbonates are very common in soils and they either form during soil formation (i.e., pedogenic) or are inherited from parent materials (i.e., detrital or lithogenic). The most common carbonates that occur in soils are calcite, Mg-calcite [$\text{Ca}_x\text{Mg}_{1-x}(\text{CO}_3)$], and dolomite. Aragonite [CaCO_3] occasionally occurs in soils and siderite has been reported to occur in some soils (3).

Carbonate dissolution and precipitation are among the most important chemical reactions in soils. Carbonates precipitate as coatings on soil particles and in soil pores that may result in cementation of particles. Other important reactions involving carbonate minerals are adsorption and/or precipitation of some anions and cations on their surfaces which has an impact on the mobility of essential plant growth elements (e.g., Fe^{2+} , Fe^{3+} , Zn^{2+} , HPO_4^{2-} , H_2PO_4^-) and elements of environmental concern (e.g., Cd^{2+} , Pb^{2+}). Carbonates (e.g., calcite, dolomite) are also added to raise the pH of acid soils (i.e., carbonates as liming agents) or to immobilize heavy metals (e.g., Pb^{2+}) in contaminated soils through precipitation of relatively insoluble carbonates (e.g., PbCO_3). These important processes have led to many studies on carbonate reactions and occurrences in soil environments.

STRUCTURE AND COMPOSITION

The carbonate ion (CO_3^{2-}) is the basic structural unit for all carbonate minerals. The large planar CO_3 group occurs as a rigid structure with the C atom occupying the center, which is surrounded by three oxygen atoms arranged in an equilateral triangle. The linkage of the carbonate group to other cations has minimal effect on the ideal C–O bond

angle of 120° in the CO_3 group (4). The nonhydrous carbonates can be grouped according to their structure into the calcite group, dolomite group, or the aragonite group (see Table 1). Hydrated carbonates have entirely different crystal structures and most crystallize in the monoclinic crystal system (Table 1).

Calcite group minerals crystallize in the hexagonal crystal system. The structure of calcite, which is the most common calcite-group mineral, is a distorted NaCl type structure where Ca alternates with CO_3 . This distorted structure places Ca atoms in a face-centered rhombohedral unit cell (Fig. 1), which is the morphologic or cleavage cell. The smaller true unit cell is an elongated rhombohedral unit cell, which is easily compared to the hexagonal unit cell (Fig. 1). Magnesite, siderite, rhodochrosite [MnCO_3], and smithsonite [ZnCO_3] are isostructural with calcite (Table 1).

Aragonite-group minerals crystallize in the orthorhombic crystal system. In this group, large divalent cations (e.g., ionic radii >0.1 nm) do not permit a stable six-fold coordination and, therefore, result in a nine-fold coordination configuration. Aragonite, which is a higher temperature and pressure CaCO_3 polymorph (calcite is the stable polymorph at room temperature), has CO_3 groups in two structural planes rather than the single structural plane of calcite. Witherite (BaCO_3), strontianite (SrCO_3), and cerussite (PbCO_3) are isostructural with aragonite (Table 1).

The third major group of carbonate minerals, the dolomite group, crystallizes in the hexagonal system. Their structure is similar to calcite-group minerals, except that different cations (e.g., Ca–Mg, Ca–Fe, Ca–Mn) alternate along the c -axis. Because of this arrangement of alternating cations, the symmetry of dolomite-group minerals is reduced compared to the calcite-group minerals. Dolomite has Ca and Mg alternating along the c -axis. Ankerite and kutnahorite [$\text{CaMn}(\text{CO}_3)_2$] are isostructural with dolomite (Table 1).

Various cations may substitute into the carbonate structure. For example, Mg^{2+} may substitute for Ca^{2+} in the calcite structure. These Mg-substituted calcites are called magnesian calcites or Mg-calcites. Mg-calcites containing up to 20 mol% MgCO_3 are found in skeletal materials of marine organisms and even higher concentrations of Mg

Table 1 Representative unit-cell formulae and selected properties of common carbonates

Carbonate group	Ideal unit-cell formula	Crystal system	Specific gravity
Calcite group			
Calcite	CaCO ₃	Hexagonal (rhombohedral)	2.71
Magnesite	MgCO ₃	Hexagonal	3.00
Siderite	FeCO ₃	Hexagonal	3.97
Rhodochrosite	MnCO ₃	Hexagonal	3.70
Smithsonite	ZnCO ₃	Hexagonal	4.43
Otavite	CdCO ₃	Hexagonal	4.96
Gaspéite	NiCO ₃	Hexagonal	4.39
Aragonite group			
Aragonite	CaCO ₃	Orthorhombic	2.95
Witherite	BaCO ₃	Orthorhombic	4.3
Strontianite	SrCO ₃	Orthorhombic	3.7
Cerussite	PbCO ₃	Orthorhombic	6.55
Dolomite group			
Dolomite	CaMg(CO ₃) ₂	Hexagonal	2.85
Ankerite	CaFe(CO ₃) ₂	Hexagonal	3.01
Kutnahorite	CaMn(CO ₃) ₂	Hexagonal	3.12
Minrecordite	CaZn(CO ₃) ₂	Hexagonal	3.45
Other carbonates			
Azurite	Cu ₃ (CO ₃) ₂ (OH) ₂	Monoclinic	3.77–3.89
Malachite	Cu ₂ CO ₃ (OH) ₂	Monoclinic	3.7–4.1
Huntite	Mg ₃ Ca(CO ₃) ₄	Hexagonal	2.70
Landsfordite	MgCO ₃ ·5H ₂ O	Monoclinic	1.69
Artinite	Mg ₂ (OH) ₂ CO ₃ ·3H ₂ O	Monoclinic	2.04
Nesquehonite	MgCO ₃ ·3H ₂ O	Monoclinic	1.84
Hydromagnesite	Mg ₅ (CO ₃) ₄ (OH) ₂ ·4H ₂ O	Monoclinic	2.25
Nyerereite	Na ₂ Ca(CO ₃) ₂	Orthorhombic	2.54
Gaylussite	Na ₂ Ca(CO ₃) ₂ ·5H ₂ O	Monoclinic	1.99
Nahcolite	NaHCO ₃	Monoclinic	2.19
Thermonatrite	Na ₂ CO ₃ ·H ₂ O	Orthorhombic	2.26
Soda (Natron)	Na ₂ CO ₃ ·10H ₂ O	Monoclinic	1.46
Trona	NaCO ₃ ·NaHCO ₃ ·2H ₂ O	Monoclinic	2.13

(Adapted from Ref. 5 and the JCPDS—International Centre for Diffraction Data).

(e.g., 45 mol% MgCO₃) in the calcite structure have been synthesized at high pressure and temperature. Most soil Mg-calcites, however, contain less than 10 mol% MgCO₃ (3). Due to the smaller ionic radius of Mg²⁺ as compared to Ca²⁺, the *a* and *c* unit cell axes decrease in length as the substitution of Mg²⁺ increases in the structure of calcite (7). Detailed discussion on the substitution of cations into carbonate structures can be found in Refs. (5, 8).

OCCURRENCE IN SOILS

Carbonates are common in many soils of the world, particularly in soils of subhumid to arid regions. Calcite is the most common carbonate in soils, but dolomite,

aragonite, and siderite are also found in certain soils. Carbonates may be either inherited into soil or form directly via precipitation processes. The most common sources and mechanisms for carbonate occurrences in soils are 1) inheritance from parent material, 2) precipitation following dissolution of soluble Ca-bearing minerals, 3) precipitation by reaction of CO₂-charged water with Ca²⁺ released by decomposition of plant residues, 4) deposition of wind-blown carbonates at the soil-surface and subsequent translocation within the soil by solution and precipitation, 5) precipitation by interaction of Ca²⁺ in rainwater entering the soil and combining with HCO₃⁻ from CO₂-charged water, 6) precipitation from CO₂-charged natural surface or irrigation water containing Ca²⁺, and 7) precipitation in soils from groundwater that has moved through carbonate-containing soils or sediments (3).

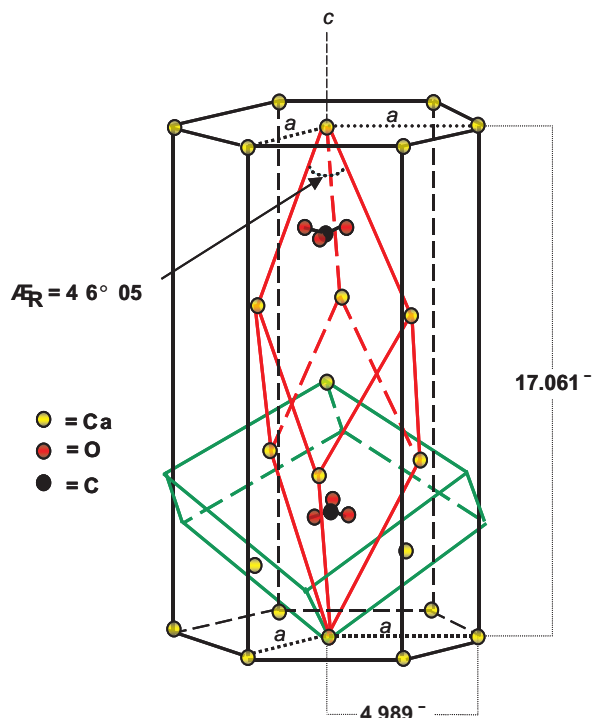


Fig. 1 Structure of calcite. Unit cell parameters for a and c are shown for the hexagonal unit cell. The elongated rhombohedral, true unit cell contains two CaCO_3 ; the two $(\text{CO}_3)^{2-}$ groups are shown ($\alpha_R = \alpha_{\text{rhombohedral-cell}}$). The morphological or cleavage cell contains four CaCO_3 (face-centered rhombohedral cell). Note that ionic radii for Ca, C, and O are not drawn to scale. (Adapted from Ref. 6.)

Calcite and Mg-calcite are the two carbonates that commonly precipitate in soils. Although all of the carbonates commonly found in soils may be inherited, aragonite and dolomite are almost always inherited. Pedogenic dolomite has been reported to occur in some saline, alkaline soils, but generally, its formation in soil is very rare (9). Mg-calcite with high MgCO_3 mole% (e.g., >10 mol%) is typically inherited in soils from marine sediments (i.e., from biogenic Mg-calcite). Siderite is relatively unstable in soil environments and is not known to form directly in soils. Magnesium carbonates are very rare in soils, but hydrated Mg carbonates (e.g., hydromagnesite, nesquehonite) may form at the surface during evaporation of solutions high in Mg^{2+} and HCO_3^- (10). Mechanisms by which carbonates precipitate in soils are provided in the following section.

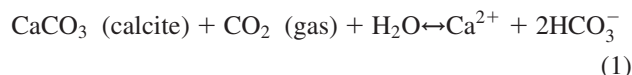
Distribution of carbonates in a soil profile depends on the climate, soil chemical properties, and degree of leaching through the profile. In many arid soils, carbonates are common secondary products in the top horizons (e.g., A and B horizons). As a general rule, carbonates tend to be

leached or removed from the upper horizons with increasing leaching or rainfall. Carbonates leached from upper horizons may precipitate as secondary carbonates in the lower horizons where they may form carbonate cemented layers (e.g., petrocalcic horizons).

Sodium carbonates may occur at the soil's surface in arid regions where soil salinity is high. Highly soluble sodium carbonates precipitate at the surface during periods of evaporation and such conditions produce soil pH values of higher than 8.5.

FORMATION

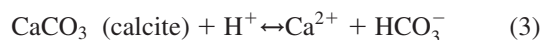
Carbonate dissolution or precipitation is dependent on several factors, such as the partial pressure of dissolved CO_2 in solution and temperature. A typical reaction for the dissolution of calcite in solution may be expressed as a function of CO_2 as:



The equilibrium constant (K^0) for this reaction at 25°C is

$$K^0 = \frac{(\text{Ca}^{2+})(\text{HCO}_3^-)^2}{P_{\text{CO}_2}} = 10^{-5.90}, \quad (2)$$

where P_{CO_2} is the partial pressure of CO_2 and brackets denote activities (11). The reaction may also be expressed as a function of H^+ as



with the respective equilibrium constant at 25°C being

$$K^0 = \frac{(\text{Ca}^{2+})(\text{HCO}_3^-)}{(\text{H}^+)} = 10^{+1.92}. \quad (4)$$

Eqs. (2) and (4) indicate that the dissolution of calcite (and other carbonates) is favored with increasing CO_2 pressure and decreasing pH. Conversely, the degassing or removal of CO_2 from solution or an increase in pH will favor calcite participation. The equilibrium pH of a solution in contact with calcite at atmospheric CO_2 pressure ($10^{-3.5}$ bar P_{CO_2}) is 8.3. Detailed discussion on carbonate solution chemistry can be found in Refs. (11, 12).

PROPERTIES

Calcium carbonate has an influence on several soil properties, e.g., soil pH, adsorption-desorption, and soil

cementation. Most soils that contain calcium carbonate will have a pH in the range of 7.1–8.5, in which the carbonate acts as a pH buffer. The surfaces of calcite are reactive and various ions may adsorb or interact at the crystal's surface. For example, Mg^{2+} , Zn^{2+} , Cu^{2+} , Fe^{2+} , and Al^{3+} may replace Ca^{2+} on exposed surface lattice sites. The reactive surfaces of carbonates may adsorb essential ions of plant such as HPO_4^{2-} , H_2PO_4^- , Fe^{2+} , Fe^{3+} , Zn^{2+} , and Mn^{2+} and adversely affect their availability for plant uptake. Iron deficiency chlorosis in plants has been attributed to the interaction of Fe and HCO_3^- in calcareous soils (13, 14). Other factors, such as quantity, mineralogy, and crystallinity of iron oxide phases in the soil, may also contribute to plant Fe chlorosis in calcareous soils (15).

Precipitation of carbonates on soil particles and in soil pores may form layers (i.e., calcic horizons) that impede the movement of water (16). Some layers may become indurated or cemented (i.e., petrocalcic horizons) and force water to move laterally in the soil.

Soil carbonates play an important role in the global carbon cycle, although their role in the greenhouse effect is not well understood (17). Soil inorganic carbon (i.e., lithogenic and pedogenic carbonates) accounts for about one-third of the total carbon in soils; the remaining two-third of soil carbon is comprised of organic carbon. Soil organic carbon is the primary C pool in humid regions, whereas carbonates are the predominant C pool in arid and semiarid regions. The role of pedogenic carbonates in atmospheric C sequestration is not clear; however, the flux of pedogenic carbonates with the atmosphere has been estimated as $0.023 \text{ Pg C yr}^{-1}$, with a turnover time in the range of 30,000–90,000 years (18).

Carbonates such as calcite have been suggested for use in the remediation of Pb-contaminated soils where Pb^{2+} reacts with HCO_3^- to form insoluble Pb carbonates. Other soil contaminants (e.g., Ba^{2+} , Cd^{2+}) may also be immobilized through carbonate precipitation with the addition of more soluble carbonate amendments (19).

In summary, carbonates are of great importance in soils because they have considerable influence on the physical and chemical properties of soils, they have an important role in the global C cycle, and, occasionally, carbonates are the predominant mineral phases that occur in soils of arid and semiarid regions.

REFERENCES

1. Reeder, R.J. Crystal Chemistry of the Rhombohedral Carbonates. In *Carbonates: Mineralogy and Chemistry*;

- Reeder, R.J., Ed.; Mineralogical Society of America: Washington, DC, 1983; 1–47.
2. Lippmann, F. *Sedimentary Carbonate Minerals*; Springer: Secaucus, NJ, 1973; 228.
3. Doner, H.E.; Lynn, W.C. Carbonate, Halide, Sulfate, and Sulfide Minerals. In *Minerals in Soil Environments*; Dixon, J.B., Weed, S.B., Eds.; Soil Science Society of America: Madison, WI, 1989; 279–330.
4. Effenberger, H.; Mereiter, K.; Zemann, J. Crystal structure refinements of magnesite, calcite, rhodochrosite, siderite, smithsonite, and dolomite with discussion of some aspects of the stereochemistry of calcite-type carbonates. *Z. Krist.* **1981**, *156*, 233–243.
5. Chang, L.L.Y.; Howie, R.A.; Zussman, J. Rock-Forming Minerals. *Non-silicates: Sulphates, Carbonates, Phosphates, Halides*, 2nd Ed.; Longman: Essex, 1996; Vol. 5B, 383.
6. Hurlbut, C.S., Jr.; Klein, C., Jr. *Manual of Mineralogy (after James D. Dana)*, 19th Ed.; Wiley: New York, 1977; 532.
7. Paquette, J.; Reeder, R.J. Single-crystal X-ray structure refinements of two biogenic magnesian calcite crystals. *Am. Mineral.* **1990**, *75*, 1151–1158.
8. Reeder, R.J. Carbonates: Mineralogy and Chemistry. *Reviews in Mineralogy*; Mineralogical Society of America: Washington, DC, 1983; Vol. 11, 394.
9. Kohut, C.; Muehlenbachs, K.; Dudas, M.J. Authigenic dolomite in a saline soil in Alberta, Canada. *Soil Sci. Soc. Am. J.* **1994**, *59*, 1499–1504.
10. Ming, D.W.; Franklin, W.T. Synthesis and characterization of lansfordite and nesquehonite. *Soil Sci. Soc. Am. J.* **1985**, *49*, 1303–1308.
11. Lindsay, W.L. *Chemical Equilibria in Soils*; Wiley: New York, 1979; 449.
12. Langmuir, D. *Aqueous Environmental Geochemistry*; Prentice-Hall: Upper Saddle Road, NJ, 1997; 600.
13. Lindsay, W.L.; Thorne, D.W. Bicarbonate ion and oxygen level as related to chlorosis. *Soil Sci.* **1954**, *77*, 271–279.
14. Inskeep, W.P.; Bloom, P.R. Soil chemical factors associated with soybean chlorosis in Calciaquolls of Western Minnesota. *Agron. J.* **1987**, *79*, 779–786.
15. Loeppert, R.H.; Hallmark, C.T. Indigenous soil properties influencing the availability of iron in calcareous soils. *Soil Sci. Soc. Am. J.* **1985**, *49*, 597–603.
16. Stuart, D.M.; Dixon, R.M. Water movement and caliche formation in layered arid and semi-arid soils. *Soil Sci. Soc. Am. Proc.* **1973**, *37*, 323–324.
17. Lal, R.; Kimble, J.M.; Eswaran, H.; Stewart, B.A., Eds. *Global Climate Change and Pedogenic Carbonates*; Lewis Publishers: Boca Raton, FL, 2000; 305.
18. Lal, R.; Kimble, J.M. Inorganic Carbon and the Global C Cycle: Research and Development Priorities. In *Global Climate and Pedogenic Carbonates*; Lal, R., Kimble, J.M., Eswaran, H., Stewart, B.A., Eds.; Lewis Publishers: Boca Raton, FL, 2000; 291–302.
19. Doner, H.E.; Grossl, P.R. Carbonates and Evaporates. In *Soil mineralogy with Environmental Applications*; Dixon, J.B., Schulze, D.G., Eds.; Soil Science Society America: Madison, WI, 2002; in press.

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